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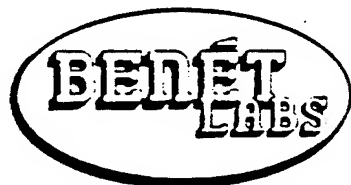
# BENÉT INTERNAL TECHNICAL REPORT

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## DETERMINATION OF PCB'S IN WATERVLIET ARSENAL MACHINE OILS BY GAS CHROMATOGRAPHY

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**Determination Of PCB's In Watervliet Arsenal Machine Oils By Gas Chromatography**

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**Abstract**

A routine method is described for screening samples of machine oils for possible polychlorinated biphenyl contamination. The method uses gas chromatography with electron capture detection. This method has proven useful at the Watervliet Arsenal for routine laboratory PCB analysis of machine oils with about two percent precision by EPA standards.

**Keywords**

chemical analyses, Watervliet Arsenal machine oils, polychlorinated biphenyls, PCB's, gas chromatography, electron capture detection

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## Introduction

Polychlorinated biphenyls (PCB's) are compounds which have been widely used in the electronics and power transmission industry as insulating materials. These compounds have been identified as environmental pollutants and are a possible health hazard. As a direct result of the concern over the presence of these materials at the Watervliet Arsenal, methods for their determination have been sought. There has been some past work on this subject that is useful for this application (ref 1,2). The procedure described here has proven useful for the determination of PCB's in machine oils used at the Arsenal.

## Approach

Strict analytical chemistry methods and procedures are followed throughout this experimental section. An excellent source of reference for these methods and procedures is by Fritz and Schenk (3).

The method uses a Perkin-Elmer Sigma 300 gas chromatograph equipped with a heated injector and a Ni63 electron capture detector capable of temperature programming. Data collection is by a Perkin-Elmer LCI-100 laboratory computing integrator.

The reagent grade materials used were hexane, Supelco Corp. Florisil and Supelco Corp. PCB standards (Aroclor # 1232, 1242, 1248, 1254, 1260 and 1262). The PCB standards each contain 1000 ppm PCB dissolved in isooctane.

The materials used are 100 ml volumetric flasks, 50 ml beakers, 10 µl syringe, 1.0 µl syringe, 1.0 ml micropipette and an eye dropper.

The gas chromatograph's initial temperature conditions are 220° C for the injector and 325° C for the detector. The temperature program for the oven is 120° C for 2 minutes, a temperature ramp of 6° C per minute for 17 minutes, and then 220° C for 11 minutes. The carrier gas is 95% argon - 5% methane with a tank pressure of 100 psi using the chromatograph's dial B set at 91. The chromatograph's range is 100 and the attenuator is 64.

Integrator conditions are the percent method, 0.00 start time, 30.00 end time, 4 peak width, 100 A sensitivity, 4 B sensitivity, 0.00 sensitivity, 2 B code, 0.0 print tolerance, 1.0 factor, 0.000 unretained peak, 0.0 area/height rejection, yes plot, 10 chart, 16 attenuator, 5 offset, yes plot retention time, no tick marks, yes plot events.

The experimental procedure requires 2 ml of oil diluted to 100 ml with hexane. If it is found after analysis that a specific sample contains a PCB concentration that is near an EPA

category borderline, it is recommended that the sample be analyzed by weight again using 2 ml of oil.

Samples proving to be visibly dirty or showing significant interferences are to be cleaned using Florisil. Cleaning consists of adding 5.0 ml (2.5 g) of Florisil to the 100 ml volumetric flask containing the sample solution in hexane. Shake the flask vigorously for one minute and allow the Florisil to completely settle out before analyzing the solution. Not allowing the complete settling of the solution may result in false positives. Florisil must be activated before use by heating it to 100° C for eight hours.

Before analyzing the samples, a standard Aroclor (ideally 1242, 1254, or 1260) should be run. A volume of 0.3 µl is injected into the chromatograph which will yield height and area data for calibration. The Aroclor standards are 1000 ppm. Additional calibration runs should be made periodically between samples.

Samples are analyzed by injecting 3.0 µl of sample solution into the chromatograph. It is extremely important to thoroughly rinse the syringe in hexane prior to drawing the actual sample into the syringe.

## Results and Discussion

Machine oils were analyzed by this procedure for Aroclors 1242, 1254, 1260, and a combination of the three as shown in Tables 1, 2, 3 and 4, respectively. These are the three most common Aroclors found to be present in Watervliet Arsenal oils. Interpretation of the results is based on inspection and evaluation of the chromatographic data.

Sample PCB concentrations may fall into three categories requiring three distinct disposal methods. The first category has less than 50 ppm PCB and is considered non-PCB containing material and can be disposed of as waste oil. The second category has 50 to 500 ppm PCB and is considered PCB contaminated material that must be disposed of by specialized incineration. The third category has more than 500 ppm PCB and is considered PCB material that must be disposed of in a strictly regulated manner.

The PCB concentration levels are calculated by selecting two characteristic peaks and standardizing those peaks for each Aroclor type. Results for each Aroclor type can then be calculated and reported if desired. Peaks are distinguished by their retention times (RT) which are directly from the chromatographs or by their relative retention times (RRT) which, for a given peak, is the retention time of the peak divided by the retention time of the non-retained peak. Relative retention times are used for the purposes of this work. Figure 1 shows the process of determining which peaks and their associated intensities are used for calculations.

Chromatographs are examined for the fingerprint patterns of the particular Aroclor type. If the chromatograph is clean and quantitative for two standard peaks then results are reportable. If the chromatographs show poor resolution, the results can be calculated on a total area basis involving all of the Aroclor peaks.

The following calculation for PCB concentration is used for the original 2 ml oil sampling:

$$\text{PCB Conc. (ppm)} = (1000 \text{ ppm})(5) \frac{(\text{Sample Peak Areas Sum})}{(\text{Standard Peak Areas Sum})} \quad (1)$$

where 5 results from a 50 sample dilution factor divided by a 10 standard/sample injection factor. This standard/sample injection factor is due to 0.3 µl standard injection and 3.0 µl sample injection.

In conclusion, the method has proven useful at the Watervliet Arsenal for routine laboratory PCB analysis of machine oils with about two percent precision by EPA standards.



**Table 1. Aroclor Standard 1242**

| <b>Peak #</b> | <b>RT<br/>(min.)</b> | <b>RRT<br/>(none)</b> |
|---------------|----------------------|-----------------------|
| 1             | 9.30                 | 21                    |
| 2             | 10.87                | 28                    |
| 3             | 11.46                | 32                    |
| 4             | 12.47                | 37                    |
| 5             | 12.83                | 40                    |
| 6             | 13.87                | 47                    |
| 7             | 14.40                | 54                    |
| 8             | 14.76                | 58                    |
| 9             | 15.76                | 70                    |
| 10            | 16.31                | 78                    |
| 11            | 16.73                | 84                    |
| 12            | 17.49                | 98                    |
| 13            | 17.78                | 104                   |
| 14            | 18.67                | 125                   |
| 15            | 19.40                | 146                   |
| 16            | 20.35                | 174                   |
| 17            | 21.22                | 203                   |
| 18            | 22.39                | 232                   |
| 19            | 23.43                | 280                   |

0.3  $\mu$ l injected

**Table 2. Aroclor Standard 1254**

| <b>Peak #</b> | <b>RT<br/>(min.)</b> | <b>RRT<br/>(none)</b> |
|---------------|----------------------|-----------------------|
| 1             | 13.78                | 47                    |
| 2             | 14.39                | 54                    |
| 3             | 14.78                | 58                    |
| 4             | 15.79                | 70                    |
| 5             | 16.34                | 78                    |
| 6             | 16.82                | 84                    |
| 7             | 17.55                | 98                    |
| 8             | 17.81                | 104                   |
| 9             | 18.70                | 125                   |
| 10            | 19.45                | 146                   |
| 11            | 19.92                | 160                   |
| 12            | 20.38                | 174                   |
| 13            | 21.24                | 203                   |
| 14            | 22.39                | 232                   |
| 15            | 23.43                | 280                   |
| 16            | 24.82                | 332                   |
| 17            | 25.93                | 372                   |
| 18            | 27.93                | 448                   |

0.3 µl injected

**Table 3. Aroclor Standard 1260**

| <b>Peak #</b> | <b>RT<br/>(min.)</b> | <b>RRT<br/>(none)</b> |
|---------------|----------------------|-----------------------|
| 1             | 15.82                | 70                    |
| 2             | 16.67                | 84                    |
| 3             | 17.71                | 104                   |
| 4             | 18.32                | 117                   |
| 5             | 18.63                | 125                   |
| 6             | 19.48                | 146                   |
| 7             | 19.87                | 160                   |
| 8             | 20.32                | 174                   |
| 9             | 21.15                | 203                   |
| 10            | 22.02                | 232                   |
| 11            | 23.37                | 280                   |
| 12            | 24.74                | 332                   |
| 13            | 25.90                | 372                   |
| 14            | 27.84                | 448                   |
| 15            | 29.78                | 528                   |

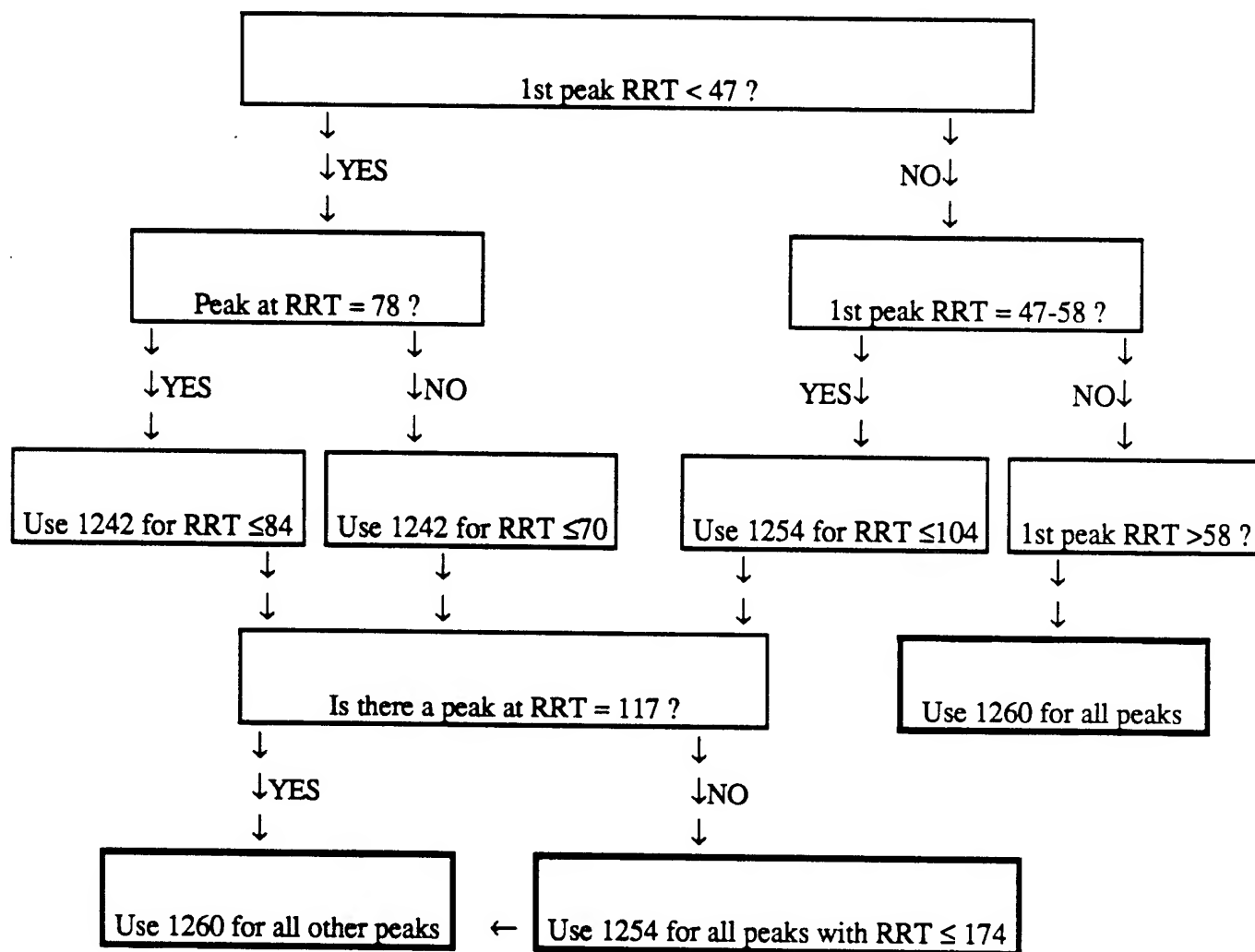
0.3  $\mu$ l injected

**Table 4. Aroclor Standard Mixture Of 1242, 1254, 1260**

| <b>Peak #</b> | <b>RT<br/>(min.)</b> | <b>RRT<br/>(none)</b> |
|---------------|----------------------|-----------------------|
| 1             | 9.39                 | 21                    |
| 2             | 10.94                | 28                    |
| 3             | 11.53                | 32                    |
| 4             | 12.52                | 37                    |
| 5             | 12.87                | 40                    |
| 6             | 13.87                | 47                    |
| 7             | 14.44                | 54                    |
| 8             | 14.81                | 58                    |
| 9             | 15.83                | 70                    |
| 10            | 16.36                | 78                    |
| 11            | 16.79                | 84                    |
| 12            | 17.55                | 98                    |
| 13            | 17.82                | 104                   |
| 14            | 18.71                | 125                   |
| 15            | 19.50                | 146                   |
| 16            | 19.95                | 160                   |
| 17            | 20.40                | 174                   |
| 18            | 21.27                | 203                   |
| 19            | 22.17                | 232                   |
| 20            | 23.53                | 280                   |
| 21            | 24.93                | 332                   |
| 22            | 26.08                | 372                   |
| 23            | 28.09                | 448                   |

0.3  $\mu$ l total injected  
(0.1  $\mu$ l each of Aroclor 1242, 1254, and 1260).

Figure 1. Peak Selection By Relative Retention Times



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